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(54) Electrochemical process for preparation of Zinc powder

(57) Disclosed is an electrochemical process for preparing zinc powder which involves: a) providing to an electrochemical cell a basic solution or suspension of zinc oxide or any other zinc compound that reacts with an aqueous base to produce zinc oxide. The basic solution or suspension is prepared by dissolving the zinc oxide or the other zinc compound in an aqueous 1.25 to 10.0 M base solution, containing at least 2 millimoles of solubilized zinc based species per 100 grams of electrolyte; and b) passing current to the cell at a current density of about 500 to about 40,000 A/m<sup>2</sup> for a time period sufficient to electrochemically reduce the zinc ox-

ide to zinc powder, wherein the electrochemical process has a current efficiency of at least 70% and is substantially free from electrode corrosion.

In one of its aspects the invention further provides for a continuous process, wherein a sufficient amount of the zinc oxide or the other zinc compound is added continuously or intermittently to the cell to maintain the concentration of the solubilized zinc based species at a level of at least 2 millimoles per 100 grams of electrolyte and at least a portion of the zinc powder formed is removed continuously or intermittently.

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## Description

## FIELD OF THE INVENTION

- 5 [0001] The present invention provides an electrochemical process, either continuous or noncontinuous, for the preparation of zinc powder from zinc oxide.

## BACKGROUND OF THE INVENTION

- 10 [0002] Zinc powder is widely used in the chemical industry in various industries. Zinc oxide containing other zinc salts, metal impurities, etc. is produced as a byproduct. Recycling of the zinc oxide to produce pure zinc powder is highly desirable from a cost as well as an environmental point of view.

- [0003] The electrodeposition of zinc metal is a well-known reaction in electrochemical technology (See, for example, D. Pletcher and F.C. Walsh, *Industrial Electrochemistry*, Blackie Academic, 1993). The electrogalvanizing of steel is a process carried out on a very large scale and aqueous acid is the normal medium. High speed, reel to reel galvanizing of steel is carried out in sulfuric acid with dimensionally stable anodes and uniform deposition is achieved at high current density by inducing very efficient mass transport by rapid movement of the steel surface. The deposition of zinc metal is also the critical electrode reaction in the electrowinning and electrorefining of zinc. In addition, there are a number of technologies, which have been demonstrated for the removal of Zn(II) from effluents. However, in these technologies, concentration of Zn(II) is low, commonly less than 100 ppm. Finally, the deposition of zinc has been widely investigated as the cathodic reaction in candidate secondary batteries. In all these applications, however, the objective is to select the conditions so as to give an adhesive and smooth zinc coating.

- [0004] Zinc powder can be produced by electrolysis either in strong alkaline or neutral zinc containing solutions. The first patents obtained on the alkaline electrolysis process date back to the early thirties (German Patents, 581013, 506590, 653557). In these methods, concentration of zinc was low (approximately 30 grams per liter) and a low current density of 1200-1500 A/m<sup>2</sup> was used. Volume efficiency and current density of these batch type processes are too low to be industrially attractive. I. Orszagh and B. Vass (Hung, *J. Ind. Chem.* (1985), 13, 287) used these methods to recycle zinc oxide byproduct from zinc dithionite production. They, however, used a divided cell at a low current density (1000-3000 A/m<sup>2</sup>). Use of a divided cell and low current density makes this process significantly more capital intensive. In their study, no significant difference was observed at different sodium hydroxide concentrations.

- [0005] For the recycling of zinc oxide containing waste by an alkaline electrolysis process to be industrially attractive, the alkaline electrolysis process needs to be improved to lower capital as well as operational expenses. Capital expenses can be significantly reduced by increasing the current density and by providing a process that is capable of being carried out in an undivided cell. Furthermore, electrolysis conditions need to be improved to achieve high volume efficiency and minimum corrosion of the electrodes. The present invention unexpectedly fulfills these and other needs.

- [0006] One advantage of the present invention is, in particular if it is carried out as a continuous process for the electrochemical reduction of zinc oxide (or any other zinc compound that reacts with an aqueous base to produce zinc oxide) to zinc powder, it provides for a very high volume efficiency. For the continuous process solid zinc oxide (or the other zinc compound) is added continuously during the electrochemical process to maintain the concentration of zinc based species (such as Zn<sup>2+</sup> ions). Furthermore, the use of high current density coupled with high volume efficiency makes the process according to the invention, and in particular the continuous process, industrially attractive.

- [0007] J. St-Pierre, D.L. Piron (Electrowinning of zinc from alkaline solutions at high current densities; *J. Appl. Electrochem* (1990), 20(1), 163-5), discloses experimental results conducted at a current density of about 2000 to 8000 A/m<sup>2</sup> to obtain cell voltage and current efficiency data necessary for specific energy computations.

- 45 [0008] U.S. Patent No. 5,958,210 discloses a method for electrowinning metallic zinc from zinc ion in aqueous solution, said method comprising performing electrolysis on a mixture of solid conductive particles and aqueous alkali solution, said solution ranging in concentration from about 3N to about 20N alkali and containing dissolved zinc ion at an initial concentration ranging from about 50 to about 500 grams of zinc ion per liter of said solution, in an electrolytic cell containing first and second vertically arranged, parallel flat plates defined as a current feeder and a counter electrode, respectively, said counter electrode coated with a substance that is catalytic for oxygen evolution, said cell further containing an ion-permeable diaphragm parallel to each of said plates and interposed therebetween to define a gap between said current feeder and said diaphragm, by passing said mixture of particles and solution through said gap such that said particles contact said current feeder and passing a current across said gap, thereby depositing metallic zinc from said solution onto said particles. The electrowinning process is disclosed to yield high current efficiency and low energy consumption. The process, however, is not industrially attractive for a large scale production of zinc powder because this process uses a relatively more complex cell, and a lower current density.

## SUMMARY OF THE INVENTION

[0009] The present invention provides an electrochemical process for preparing zinc powder, which comprises the steps of:

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a) providing to an electrochemical cell a solution or suspension in an aqueous 1.25 Molar to 10.0 Molar base solution of zinc oxide or any other zinc compound that reacts with an aqueous base to produce zinc oxide, the solution or suspension containing at least 2 millimoles of solubilized zinc based species per 100 grams of electrolyte; and

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b) passing current to the cell at a current density of about 500 to 40,000 A/m<sup>2</sup>, for a time period sufficient to electrochemically reduce the zinc based species to zinc powder,

wherein in steps a) and b), the electrolyte consists of the aqueous base solution and the zinc oxide or the other zinc compound, and the solubilized zinc species are derived from the zinc oxide or the other zinc compound.

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[0010] For carrying out the process of the invention in a continuous way, a sufficient amount of the zinc oxide or the other zinc compound is continuously or intermittently added to the cell to maintain the concentration of the zinc based species at a level of at least 2 millimoles per 100 grams of electrolyte and at least a portion of the zinc powder formed is continuously or intermittently removed.

## 20 DESCRIPTION OF THE PREFERRED EMBODIMENTS

[0011] The first step a) of the presently claimed electrochemical process for preparing zinc powder involves: providing to an electrochemical cell a solution or suspension in an aqueous 1.25 Molar to 10.0 Molar base solution of zinc oxide or any other zinc compound that reacts with an aqueous base to produce zinc oxide, the solution or suspension containing at least 2 millimoles of solubilized zinc based species per 100 grams of electrolyte.

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[0012] As used herein, the phrase "zinc powder" encompasses zinc metal particles of various particle sizes known to one of ordinary skill in the art and is not limited to fine particles.

[0013] The electrolytic cell employed in the present invention may be an undivided or divided cell, with the undivided cell being preferred. Use of an undivided cell requires lower capital. Furthermore, operational costs are also lower when an undivided cell is used. Therefore, it is important that the process be capable of being carried out in an undivided cell.

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[0014] Since zinc powder formed at the cathode by the reduction reaction can react with the oxygen generated at the anode, cathodic and anodic chemistries are generally separated by some kind of a porous diaphragm which allows the current to pass, but suppresses mixing of anolyte and catholyte. Cells of this kind are called divided cells.

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[0015] The design of the undivided cell is simpler and the cell voltage required to achieve the desired current density is lower because of the lower ohmic resistance. This means that the electrical cost is generally lower where an undivided cell is used. Furthermore, capital cost required with the undivided cell is significantly lower than the divided cell.

[0016] The anode may be made from any conventional suitable material such as platinum, or iridium, either of which may be coated over an inert support such as niobium or titanium. The anode may also be made of nickel, or from conventional materials having good alkali corrosion resistance, e.g., lead or stainless steel. The cathode may be made from any conventional suitable materials having good alkali corrosion resistance, such as magnesium nickel, lead and stainless steel. Preferably, the anode in the present invention is formed of stainless steel and the cathode is formed of stainless steel, magnesium, or magnesium alloy.

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[0017] The solubilized zinc based species are obtained by dissolving zinc oxide, or the other zinc compound (such as zinc sulfate) in an aqueous 1.25 M to 10.0 M, preferably 2.5 to 8.0 M base solution, in one embodiment 2.5 M to 5.0 M base solution, and in one embodiment 5.0 to 10.0 M base solution, and in one embodiment 8.0 to 10.0 M base solution.

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[0018] For the continuous process a high concentration (preferably obtained from a saturated solution of, or a light slurry of zinc oxide) of the solubilized zinc based species in the electrolyte is maintained during the electrolysis by adding ZnO or the other zinc compound either continuously or intermittently during the electrolysis.

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[0019] Examples of solubilized zinc based species include  $\text{ZnO}_2^{2-}$ ,  $\text{HZnO}_2^{-}$ ,  $\text{Zn(OH)}^{+}$ , and  $\text{Zn}^{2+}$ . Zinc oxide is known to dissolve by reacting with water to form a variety of species (which includes ionic and neutral species) depending upon pH. Thus a solution of zinc oxide in alkaline solution may contain species such as  $\text{ZnO}_2^{2-}$ ,  $\text{HZnO}_2^{-}$ ,  $\text{Zn(OH)}_2$ ,  $\text{Zn(OH)}^{+}$ , and  $\text{Zn}^{2+}$ . Therefore, solubilized zinc based species may comprise one or more of these species in the solution.

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[0020] The concentration of solubilized zinc based species provided to the electrochemical cell is at least 2 millimoles (mmoles) per 100 grams (g) of electrolyte. The electrolyte comprises the aqueous 1.25 Molar to 10.0 Molar base solution and the zinc oxide or the other zinc compound. Preferably, the concentration of the solubilized zinc based

species is at least 20 mmoles per 100 grams of electrolyte, and in one embodiment at least 30 mmoles per 100 grams of the electrolyte, and in one embodiment ranges from 2 to 120 mmoles per 100 grams of the electrolyte. By way of example, 2 weight percent of zinc oxide in the electrolyte corresponds approximately to 30 mmoles of solubilized zinc based species per 100 grams of the electrolyte. Also by way of example, 2 millimoles of zinc based species per 100 grams of electrolyte could be provided by dissolving 0.16 grams ( $0.002 \times 81.37 = 0.16$ ) of zinc oxide in 99.84 grams of the 1.25 M to 10.0 M aqueous base solution.

[0021] Concentration of the aqueous base solution (such as caustic solution) should be as high as possible because of the higher solubility of zinc oxide in more concentrated aqueous base solutions. In order to achieve high current density (which is a function of the concentration of the electroactive species such as zinc based species), high current efficiency, and high volume efficiency (i.e., high amount of zinc produced per volume unit of electrolyte) it is desirable to use the electrolytes containing high concentration of solubilized zinc based species. Because of the higher solubility of zinc oxide in stronger base solutions, higher concentration of solubilized zinc based species is achieved by using stronger base solutions. By maintaining a light suspension of zinc oxide during the electrolysis in the present invention, the concentrations of solubilized zinc based species during the electrochemical process can be kept as high as possible. However, the concentration of solubilized zinc based species can be increased by using a stronger initial base solution used for solubilizing zinc oxide. It is generally believed that a higher concentration of base solution is favorable for minimizing corrosion of the anode.

[0022] However, it has been unexpectedly found that high concentration (such as concentration significantly higher than 10.0 M) of base (e.g., NaOH solution) solution causes an adverse effect on corrosion of the stainless steel anode and on the current efficiency of the process, especially where electrolysis is carried out at high current densities (such as higher than 10,000 A/m<sup>2</sup>). This adverse effect is minimized by lowering the aqueous base concentration. The most preferred concentration of the aqueous base in the present invention is 3.0 to 8.0 M, even more preferred 5.0 M.

[0023] The aqueous base solutions employed in the process of the invention are prepared by combining water with a source of alkali metal or alkaline earth metal ions, such as lithium sodium and potassium, and a source of hydroxyl (OH<sup>-</sup> ions). A single source may of course provide both types of ions. The various alkali or alkaline earth metal ions are preferably supplied from various compounds such as hydroxides and oxides. Preferred base solutions are sodium and potassium hydroxide solutions.

[0024] The solubility of zinc oxide in the aqueous base solution is limited, and depends on the temperature. The present invention envisions use of the zinc oxide at any range of concentrations in which it is soluble in the aqueous base solution. However, the concentration of the electroactive species -in this case solubilized zinc based species-is a major variable that determines the maximum feasible current density at which zinc is electrodeposited at maximum current efficiency. An excessive current density will generally lead to secondary reactions such as hydrogen evolution (with a potential for some safety problems). Thus, too low a concentration of zinc based species in the electrolyte at high current densities will lead to lower current efficiency and hence is undesirable from cost and safety considerations.

[0025] Hence, in the present invention, if carried out as a continuous process, a saturated solution or a light suspension of zinc oxide (or the other zinc compound that produces zinc oxide upon reaction with aqueous base) is maintained.

[0026] In one embodiment, the zinc oxide or the other zinc compound which produces the zinc oxide is present in the aqueous base in an amount of 0.15 to 12 weight percent (wt.%), preferably 1 to 9 wt.%, in one embodiment from 1.5 to 6 wt.% all calculated at 90°C, based on the weight of the electrolyte. At 90°C, a saturated solution of zinc oxide in 4.0 M NaOH contains 2 wt% of zinc oxide, based on the total weight of the electrolyte.

[0027] The second step b) of the presently claimed invention involves passing current to the cell at a current density of 500 to 40,000 amps per square meter (A/m<sup>2</sup>), preferably 1,000 to 40,000 A/m<sup>2</sup>, in one embodiment from 1000 to 5,000 A/m<sup>2</sup>, and in one embodiment from 10,000 to 15,000 A/m<sup>2</sup>, and in one embodiment, 10,000 to 20,000, and in one embodiment, from 15,000 to 20,000 A/m<sup>2</sup>, and in one embodiment 20,000 to 30,000, and in one embodiment, 30,000 to 40,000 A/m<sup>2</sup>, and in one embodiment 10,000 to 40,000 A/m<sup>2</sup>, for a time period sufficient to electrochemically reduce the solubilized zinc based species to zinc powder.

[0028] If the process is carried out as a continuous process, a sufficient amount of zinc oxide or the other zinc compound is added to the cell continuously or intermittently while current is passed to the cell to maintain the concentration of the solubilized zinc based species at a level of at least 2 mmoles of solubilized zinc based species per 100 grams of the electrolyte. Also, while current is passed to the cell, at least a portion of the zinc powder formed is removed continuously or intermittently.

[0029] While the present invention is not limited in scope by current efficiency considerations, in one embodiment, the present electrochemical process has a current efficiency of at least 70% (i.e., current efficiency of 70-100%), in one embodiment at least 80%, and in one embodiment at least 90%. Electrolysis of a basic zinc solutions containing approximately 1% zinc ions at a current density as high as 20,000 A/m<sup>2</sup> produce zinc at a current efficiency of 75 to 85%.

[0030] As used herein, the phrase "current efficiency" is the ratio, generally expressed as a percentage, of the actual zinc deposition rate to the rate which would be achieved if all of the current passing through the cell were consumed by reduction of zinc ion. The current efficiencies in zinc electrowinning cells are typically less than 100% because of

the concurrent reduction of water to hydrogen gas, competing with the reduction of the solubilized zinc based species (e.g., from zinc oxide) to zinc metal at the cathode.

[0031] For electrolysis, temperatures higher than ambient are generally desired because of the beneficial effects on the kinetics of all steps in an electrode process. At higher temperatures, the diffusion coefficient, the exchange current density and the rates of chemical reactions generally are increased. The decrease in viscosity and increase in diffusion coefficient leads to the increased mass transport rates. This increased mass transport of zinc species from the bulk of the solution to the cathodic region is highly desirable. However, increase in the rate of chemical reaction such as the oxidation of zinc produced with oxygen and mass transport of the byproduct oxygen to the bulk of the solution may not be desirable. In the present invention, higher than ambient temperatures are found to be favorable for the electrolytic reduction of zinc oxide to zinc, and are thus preferred.

[0032] Thus, in one embodiment, the presently claimed electrochemical reduction process is conducted at a temperature of from 30°C to 120°C, preferably from 50°C to 110°C, and more preferably from 70°C to 100°C, most preferably from 80° to 95°C.

[0033] In one embodiment of the present invention, the electrochemical process is substantially free of electrode corrosion. As used herein, the phrase "substantially free of electrode corrosion" encompasses corrosion levels, expressed as milligrams of electrode metal lost to corrosion/mole of electrons passed of 100 or less (i.e.  $\leq 100$  mg/mole of electrons). In one embodiment, the corrosion levels are less than or equal to 50 mg/mole of electrons, and in one embodiment less than or equal to 40, 30, 20, 10, and 5 mg/mole of electrons. Methods for measuring corrosion levels will be known to one of ordinary skill in the art. In one embodiment, as in the present invention, it is measured by analysis of the recovered zinc powder for iron ion concentration by atomic absorption spectroscopy or inductively coupled plasma, as iron lost by corrosion is insoluble in the aqueous base solutions of the present invention.

[0034] The following specific examples will provide detailed illustrations of the methods of producing and utilizing compositions of the present invention. These examples are not intended, however, to limit or restrict the scope of the invention in any way and should not be construed as providing conditions, parameters or values which must be utilized exclusively in order to practice the present invention. Unless otherwise specified, all parts and percents are by weight.

#### EXAMPLES

[0035] General procedures 1, 2, or 3 are used for the following examples for the electrolytic reduction of zinc oxide to zinc powder in either the continuous or noncontinuous process. For the continuous process additional zinc oxide is added to the cell during the electrolysis and at least a portion of the zinc deposited on the cathode is removed periodically.

##### General procedure 1:

[0036] In these experiments, a 4-liter (L) resin Kettle (4 inch in diameter and 18 inch high) is used as the cell. A saturated solution of zinc oxide in the aqueous sodium hydroxide solution (3 to 3.5 liters) at 50 to 80°C is charged into the resin kettle. A thermometer, stainless steel cathodes and anodes are positioned in the cell using laboratory clamps. Mixing is achieved by pumping (a centrifugal pump March #BC-3C-MD is used) the solution of ZnO from the bulk of the solution to the region between cathodic and anodic plates. Parts of the cathode and anode surfaces are covered with Teflon tape to achieve the desired active cathode and anode surface areas. Electrolysis is carried out at various current densities and the number of coulombs passed is measured by using a digital coulometer. At the end of the experiment, zinc particles are separated from the electrolyte by decantation, washed with water and then dried. Dried zinc particles were analyzed to determine the zinc content.

##### General procedure 2:

[0037] Same as general procedure 1, except that a gear pump (Micropump #GL-H23FFSE) is used to mix the ingredients in the cell.

##### General procedure 3:

[0038] Same as general procedure 1, except that mechanical stirring (rather than pumping of solution) is used to mix the ingredients in the electrochemical cell.

#### Example 1-10

[0039] The results of electrolysis of zinc oxide in a noncontinuous process under various conditions using general

procedure 1 or 3 are shown below in Table 1.

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TABLE 11

Exp. No.	[NaOH] <sup>2</sup> (M)	Initial # moles of zinc ions in electrolyte	Moles of electrons passed	Temp. (°C)	Current Density (A/m <sup>2</sup> )	Zn produced (moles)	Current Efficiency (%)	Anode Corrosion (mg lost/mole electrons)	General Procedure
1	8.0	3.7	2.50	52-75	19375	0.93	75	34	1
2	19.0	4.6	2.50	80-81	19375	0.17	14	1076	1
3	4.0	1.0	1.76	63-66	21053	0.67	76	6	1
4	4.0	1.1	1.87	74-78	19375	0.80	86	1	1
5	4.0	1.0	1.76	57-62	20202	0.75	86	3	3
6	4.0	1.0	1.77	79-90	29206	0.73	83	1	3
7	8.0	2.6	4.65	79-80	10159	2.02	87	10	3
8	2.8	0.43	0.73	55-67	10159	0.13	34	1	3
9	19.0	5.17	3.10	74-75	1491	1.13	72	173	3

<sup>1</sup>In all these experiments, stainless steel (316 stainless steel) electrodes (anode and cathode) are used. Inter electrode distance is 2 cm.

<sup>2</sup>Concentration of NaOH before ZnO is dissolved in it.

[0040] In the above experiments (Table 1), in general, when mass transport is achieved by pumping (general procedure 1) the electrolyte solution from the bulk to the cathodic region, a lower current efficiency is observed than when mechanical stirring (general procedure 3) is used for mass transport (compare Exp. 3 vs. Exp. 5, Table 1). While not wishing to be bound by theory, it is believed that this is caused by the greater mixing of the zinc produced at the cathode with the oxygen produced at the anode caused by the centrifugal pump compared to mixing by mechanical stirring.

[0041] The unexpected results of the present invention can be understood from the following discussion: Electrochemical recycling of zinc oxide byproduct to zinc powder suffers from its poor solubility in base solution. Solubility increases with increased base solution. One way to increase zinc ion concentration is to increase the concentration of the base solution. Furthermore, a greater concentration of zinc ions is expected to improve mass transport of zinc ions to the cathode and hence the current efficiency of the electrodeposition of zinc.

[0042] Surprisingly it has been found that electrolysis of a solution with increased concentration of zinc based salt, where a 19 M base solution is used to dissolve zinc oxide to achieve a higher concentration of zinc based salts, results in poorer current efficiency when a current density of 19375 A/m<sup>2</sup> is used. (See Exp. 2 versus Exp. 1, Table 1). Such a result is surprising in view of the prior art (See, e.g., I. Orszagh and B. Vass, *Hung. J. Ind. Chem.*, 13, (1985) 287 and U.S. Patent 5,958,210). In view of such an unexpected finding, it has been found a range of base concentrations (2.5 M to 10.0 M), wherein the electrochemical process can be carried out at high current densities (10,000 to 40,000 A/m<sup>2</sup>) and current efficiencies (70-100%).

[0043] Use of stainless steel anode under alkaline conditions is not expected to result in corrosion of the anode. Corrosion generally takes place if protons generated at the anode are not neutralized. High base (e.g., NaOH) concentration is expected to neutralize these protons more efficiently and hence corrosion under high base concentration should be even lower than under lower base concentration. However, the data in Table 1 surprisingly shows that corrosion with a 19 M caustic solution (Exp. 2) is dramatically more than corrosion with an 8 M (Exp. 1) caustic solution.

#### Example 10-19

[0044] The results of electrolysis of zinc oxide in a continuous process under various conditions using general procedure 1, 2, or 3, wherein additional zinc oxide is added to the cell during the electrolysis and at least a portion of the zinc deposited on the cathode is removed periodically, are shown below in Table 2.



Table 21

Exp No.	NaOH <sup>2</sup> (M)	Moles ZnO added during electrolysis <sup>3</sup>	Concentration of solubilized zinc based species (mmoles/100g electrolyte) <sup>4</sup>	Moles of electrons passed	Temp (°C)	Current Density (A/m <sup>2</sup> )	Zn produced (moles)	Current Efficiency (%)	Anode Corrosion (mg lost/mole electrons)	General Procedure
10	4.0	1.23	24	2.48	73-78	19375	1.18	95	37	1
11	1.3	1.46	2	3.12	60-74	21053	0.79	51	6.3	1
12	2.8	1.77	12	6.55	63-69	20192	1.57	48	8.5	1
13	4.0	2.11	24	6.07	57-66	20192	2.22	73	33	2
14	4.0	10.69	24	22.55	76-96	18849	10.74	95	2	3
15	4.0	1.28	24	3.03	66-93	29206	1.52	100	1	3
16	4.0	1.64	24	2.90	81-109	35185	1.40	96	2	3
17	4.0	1.59	24	3.21	55-78	1500	1.47	91	4	3
18	1.3	1.03	2	3.35	69-84	1500	0.93	56	2	3
19	10.0	1.54	100	2.69	74-89	20317	1.26	94	79	3

<sup>1</sup>In all these experiments, stain steel (316) anode and cathode are used. Inter electrode distance is 2 cm.<sup>2</sup>Concentration of NaOH before ZnO is dissolved in it.<sup>3</sup>Initial electrolyte is a saturated solution of ZnO in aqueous base solution<sup>4</sup>These concentrations are approximate values only.

[0045] In the above experiments, in general, current efficiency is lower when mass transport is achieved by a gear pump (general procedure 2) rather than a centrifugal pump (general procedure 1) or by mechanical stirring (general procedure 3) (Compare Exp. 13 with Exp. 10 and 14). While not wishing to be bound by theory, it is believed that this is caused by the greater mixing of the zinc produced at the cathode with the oxygen produced at the anode in the case of mixing by the gear pump than in mixing by the centrifugal pump or mechanical stirring.

[0046] The volume efficiency advantages of a continuous process over a corresponding noncontinuous solution process is illustrated by comparing Example 14 in Table 2 above with Example 5 in Table 1 above. The maximum volume efficiency (assuming that all of the zinc based species in the solution has been reduced to zinc powder) for the noncontinuous solution process is 2.13 g of zinc per 100 milliliter (ml) of the electrolyte, while the continuous process, corresponding to Example 14 in Table 2 above has an intermittent volume efficiency (defined as the volume efficiency obtained after the electrolysis is terminated subsequent to passing the desired charge through the cell) of 23.5 g of zinc per 100 ml of electrolyte after passing 22.5 moles of electrons (2,175,600 coulombs). The theoretical volume efficiency of the continuous process may approach infinity since, zinc oxide is being supplied continuously in the continuous process.

[0047] Each of the documents referred to above is incorporated herein by reference in its entirety, for all purposes. Except in the Examples, or where otherwise explicitly indicated, all numerical quantities in this description specifying amounts and concentrations of materials, reaction and process conditions (such as temperature, current density, current efficiency), and the like are to be understood to be modified by the word "about".

[0048] While the invention has been explained in relation to its preferred embodiments, it is to be understood that various modifications thereof will become apparent to those skilled in the art upon reading the specification. Therefore, it is to be understood that the invention disclosed herein is intended to cover such modifications as fall within the scope of the appended claims.

## Claims

1. A electrochemical process for preparing zinc powder which comprises the steps of:

- a) providing to an electrochemical cell a solution or suspension in an aqueous 1.25 Molar to 10.0 Molar base solution of zinc oxide or any other zinc compound that reacts with an aqueous base to produce zinc oxide, and
- b) passing current to the cell at a current density of about 500 to 40,000 A/m<sup>2</sup>, for a time period sufficient to electrochemically reduce the zinc based species to zinc powder,

wherein the electrochemical process has a current efficiency of at least 70% and is substantially free from electrode corrosion.

and wherein in steps a) and b), the electrolyte comprises the aqueous base solution and the zinc oxide or the other zinc compound.

2. The process of claim 1, wherein the electrochemical cell has a stainless steel or nickel anode.

3. The process of claim 1 or 2, wherein the electrochemical cell has a magnesium or magnesium alloy cathode.

4. The process of claims 1 to 3, wherein the aqueous base solution comprises ions of at least one alkali or alkaline earth metal selected from sodium, potassium, and mixtures thereof which are provided in the form of hydroxides and/or oxides.

5. The process of claim 4, wherein the compound is selected from sodium hydroxide and potassium hydroxide.

6. The process of claims 1 to 5, wherein in step a), the solubilized zinc based ions comprise at least one member selected from the group consisting of  $\text{ZnO}_2^{2-}$ ,  $\text{HZnO}_2^+$ ,  $\text{Zn(OH)}^+$ , and  $\text{Zn}^{2+}$ .

7. The process of claims 1 to 6, wherein in step a), the zinc oxide or the other zinc compound is present in an amount of up to 12 wt.% calculated at 90°C, based on the weight of the electrolyte.

8. The process of claim 7, wherein in step a), the zinc oxide or the other zinc compound is present in the basic solution in an amount of 1 to 9 wt.% calculated at 90°C, based on the weight of the basic solution.

9. The process of claims 1 to 8, wherein step b) is carried out at a temperature range of from 30 to 120°C.

10. The process of claim 9, wherein step b) is carried out at a temperature range of from 80 to 95°C.
11. The process of claims 1 to 10, wherein step (b) has a current efficiency of at least 70%.
- 5 12. The process of claims 1 to 11, wherein the electrode corrosion is corrosion of the anode and is less than or equal to 100 milligrams of lost anode metal/mole of electrons.
13. The process of claims 1 to 12, wherein in step a), the concentration of the solubilized zinc based species is 2 to 120 mmoles per 100 grams of the electrolyte.
- 10 14. The process of claims 1 to 13, wherein in step a), the aqueous base solution has a concentration of 1.25 to 10 M.
15. The process of claim 14, wherein in step a), the aqueous base solution has a concentration of 3.0 to 8.0 M.
- 15 16. The process of claims 1 to 15, wherein in step b), the current density is in the range of 1.000 to 40.000 A/m<sup>2</sup>.
17. The process of claims 1 to 16, wherein the electrochemical cell is an undivided cell.
18. The process of claim 1 to 17, **characterized in that** the process is a continuous process additionally comprising  
20 the steps of continuously or intermittently adding a sufficient amount of zinc oxide to the cell to maintain the concentration of the solubilized zinc based species at a level of at least 2 mmoles per 100 grams of electrolyte, and continuously or intermittently removing at least a portion of the zinc powder formed.
19. A continuous electrochemical process for preparing zinc powder according to claim 18 which comprises the steps  
25 of:
  - a) providing to an electrochemical cell a solution or suspension of zinc oxide in an aqueous 1.25 Molar to 10.0 Molar base solution, the solution or suspension of zinc oxide containing at least 2 millimoles of solubilized zinc based species per 100 grams of electrolyte; and
  - 30 b) passing current to the cell at a current density of 500 to 40.000 A/m<sup>2</sup>, for a time period sufficient to electrochemically reduce the solubilized zinc based species to zinc powder, while continuously or intermittently adding a sufficient amount of zinc oxide to the cell to maintain the concentration of the solubilized zinc based species at a level of at least 2 mmoles per 100 grams of electrolyte, and continuously or intermittently removing at  
35 least a portion of the zinc powder formed;
- wherein in steps a) and b), the electrolyte comprises the aqueous base solution and the zinc oxide or the other  
zinc compound.



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## EUROPEAN SEARCH REPORT

Application Number  
EP 02 40 5066

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